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(21) International Application Number: PCT/GB98/03426 (22) International Filing Date: 12 November 1998 (12.11.98) (30) Priority Data: 9723818.2 12 November 1997 (12.11.97) GB (71) Applicant (for all designated States except US): ECC INTERNATIONAL LTD. [GB/GB]; 1015 Arlington Business Park, Theale, Reading, Berkshire RG7 4SA (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): KOSTUCH, Jacek, Antoni [GB/GB]; 24 Manor View, Par, Cornwall PL24 2EN (GB). (74) Agent: McCORMACK, Derek, James; ECC International Ltd., Patents Dept., John Keay House, St. Austell, Cornwall PL25 4DJ (GB).		(81) Designated States: AU, BR, CN, UA, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>

(54) Title: TREATMENT OF MINERAL PARTICLES**(57) Abstract**

A method of heat treating kaolin particles which includes the steps of establishing in a furnace a heating zone suitable to calcine the particles and passing the particles rapidly through the heating zone whereby the particles are flash calcined in the heating zone, wherein the furnace is of the kind in which a toroidal fluid flow heating zone is established and the particles are heated in the said heating zone to a temperature of at least 550 °C but not greater than 1100 °C by application to the particles of a temperature increase rate greater than 10³ Celsius degrees per second to give a rapid blistering of the particles caused by rapid dehydroxylation of the kaolin and wherein the particles have a residence time of less than 1 second in the said toroidal fluid flow heating zone.

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TREATMENT OF MINERAL PARTICLES

The present invention relates to the treatment of mineral particles. In particular, it relates to the
5 heat treatment by flash calcining of mineral particles suitable to be employed as coating, filler and extender materials in products such as papers, polymers, paints, cements, concretes and the like. Such minerals include, for example, clays especially kaolins
10 processed or produced by various processes such as grinding or precipitation.

Calcination is a known process wherein particles of a material, eg mineral, are heated. In flash calcining the particles are heated extremely quickly,
15 almost instantaneously. In contrast, in the alternative process of soak calcining heating is carried out at a more gentle rate.

Prior art methods of flash calcining have one or more disadvantages. For example, in fluid bed type
20 furnaces it is necessary, in order to treat certain feed particulate materials, to establish an inert coarse particle bed in the furnace before introduction of the feed material to ensure efficient heating of the feed material. Also, if the feed material contains
25 fluxing agents there is a likelihood above a certain temperature, eg 900°C, that fluxed material will build up on the resident bed causing efficient operation of the system to be hindered or, eventually, the system to stall.

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In other cases, the particles come into direct contact with combusting fuel. Particles passing through the hottest part of the flame tend to be overheated which can cause the product to be abrasive.

- 5 Also it is difficult to ensure that the particles are all treated at a uniform temperature and product quality is difficult to control.

- In still further prior art methods, the flash calcination treats only the exterior parts of the particles and a further calcination step, with considerable expense, is required to give suitably complete flash calcination of the particles.

- In any case, it is desirable to improve certain product properties compared with those obtained using the prior art methods.

It is an object of the present invention to carry out flash calcining of mineral particles by a method which reduces or eliminates the above disadvantages and which provides improved product properties.

- 20 According to the present invention in a first aspect there is provided a method of heat treating kaolin particles which includes the steps of establishing in a furnace a heating zone suitable to calcine the particles and passing the particles rapidly through the heating zone whereby the particles are flash calcined in the heating zone, wherein the furnace is of the kind in which a toroidal fluid flow heating zone is established and the particles are heated in the said heating zone to a temperature of at least 550°C by

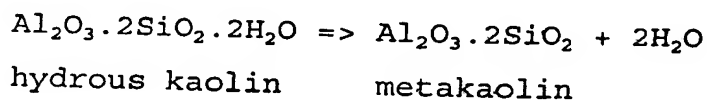
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application to the particles of a temperature increase rate greater than 10^3 Celsius degrees per second to give a rapid blistering of the particles caused by rapid dehydroxylation of the kaolin and the particles
5 have a residence time of less than 1 second in the said toroidal fluid flow heating zone.

Furnaces of the toroidal fluid flow kind are known per se. Such furnaces are described for example in USP 4,479,920 and WO98/03256. Usually, a hot gas is passed
10 through gaps between angled blades or vanes in a ring of blades or vanes provided in the operational chamber or reactor part of the furnace. The blade ring is formed in an annular gap between the wall of the chamber and a central block, eg an upwardly pointing
15 conical portion, located on the axis of the chamber. Gas flow is caused to follow a rotary path in a doughnut shaped region around the block and in individual swirls within the rotary path. This provides heat transfer to material, eg particulate
20 material, to be heated in the gas flow.

Although heating of particulate materials in a toroidal fluid flow heating device is well known and use of such a device has been mentioned for heat treatment of kaolin in WO98/03256, such devices are not
25 used industrially in the kaolin industry for kaolin treatment. Use of such a device to provide flash calcining of kaolin in accordance with the invention and the benefits to be obtained have not previously been suggested.

The transformations of kaolinite (the principal constituent of kaolin) on heating are known. A significant peak in the differential thermal analysis at 550-650°C denotes the formation of metakaolin from
5 hydrous kaolin by a hydroxylation reaction:



10 This is a strongly endothermic reaction and it is the evolution of water of which use is made to give flash calcined kaolin unique properties as follows.

 During flash calcination, kaolin particles are subject to extreme temperature gradients, eg from
15 ambient to 550°C or higher in fractions of a second. This causes the water vapour generated from the reaction to expand extremely rapidly, in fact faster than it can diffuse through the crystal structure of the particle. The pressures generated are sufficient
20 to produce sealed voids as the interlayer hydroxyl groups are driven off, and it is these swollen interlayer spaces, or voids or blisters, between the kaolin platelets, which typify flash calcined kaolins and give them their characteristic properties, as
25 described later.

 Thus, in the method of the present invention the kaolin particles are heated to a temperature greater than 550°C, preferably a temperature in the range 800°C to 1100°C, more preferably 900°C to 1050°C, preferably

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950°C to 1000°C, by application to the particles of a temperature increase rate greater than 10^3 Celsius degrees per second, eg at least 5×10^3 Celsius degrees per second, in some cases at least 10^4 Celsius degrees per second, whereby rapid dehydroxylation to give the required blistering effect described above.

The delivery of mineral particles into the toroidal fluid flow heating zone in the method according to the first aspect of the present invention is desirably carried out by injection of the particles dispersed from one another in a carrier fluid. This ensures that the particles are not in contact with one another when they are rapidly heated in the toroidal fluid flow. Such contact can cause fluxing and fusing of particles and leads to a product which can be abrasive. Such abrasiveness is undesirable. For example, where the product is to be employed in paper making, eg as a coating or filler material, it can harm the paper making machinery.

The carrier fluid may comprise a gas such as air or inert gas which may be initially blown over a source of the particles to be suspended in it or to which the particles may be added to carry them into the furnace. The carrier fluid may be at ambient temperature eg a temperature of from 15°C to 30°C although it could if required be heated.

The rate at which heat is transferred from carrier fluid to entrained particles is largely dependent on the boundary layer which surrounds each particle. This

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boundary layer is an envelope of carrier fluid which is stationary relative to the particle and which acts as an insulator, thus limiting heat transfer rate. If this layer can be disrupted, faster heat transfer will occur. Relative motion between the air and particle causes an increase in heat transfer due to convection and a decrease in the depth of the stationary air layer. For particle Reynolds numbers in the range 20-2,000 the following equation is applicable:

10

$$Nu = 2 + 0.69Re^{0.5}Pr^{0.33}$$

where: the Nusselt number, $Nu = hd/k$
the Reynolds number, $Re = \rho u d / \mu$
and the Prandtl number, $Pr = c_p \mu / k$

15

This means that as the relative velocity (u) between the carrier gas and the particle increases, the heat transfer coefficient (h) rises due to a decrease in thickness of the boundary layer. The required relative velocity can be obtained by use of the toroidal fluid flow heating device.

20

By suspending particles in jets of hot air, which may be formed in the fluid flow heating zone, where much of the high velocity component is in the horizontal plane, it is possible to subject particles to impact velocities in excess of their terminal velocity. This allows very efficient heat transfer whilst retaining sufficient residence time in the reactor for the entire particle size range of the

25

kaolin particles to undergo the required dehydroxylation reaction.

The required rapid heating temperature gradient may be achieved by adjustment of the temperature of the heating zone of the furnace and the rate at which gas to form the toroidal fluid flow heating zone is delivered to the heating chamber of the furnace and/or the rate at which the particles to be heated are delivered into the chamber and/or the rate at which calcined particles are extracted from the chamber. The operational controls of the furnace as supplied by the manufacturer can suitably be adjusted to give the required gradient. The furnace may for example be a TORBED[®] 400 reactor supplied by Torftech Ltd, Mortimer UK adapted to operate at higher temperatures as described in WO98/03256.

The mineral particles are preferably dispersed in a minimum amount of suspending fluid, eg air, to give efficient heating of the particles in the flash calcination process. Preferably, the density of the particles in the carrier fluid is as high as possible without the particles having substantial contact with one another when injected into the heating zone. The particles to be delivered into the heating zone of the furnace may be suspended in a flow of fluid, eg air, by use of a pressurised chamber. Kaolin particles contained in such a chamber may be forced at an adjustable rate from the chamber into a rotating member, eg disc, whose speed of rotation can be

adjusted to give a required flow rate and density. A distributor may be employed to distribute a flow of the particles in fluid from a single source into the heating chamber of the furnace via a plurality of inlet delivery conduits. The particle flow may be designed in accordance with techniques well known in the pneumatic conveyance of particulate materials, eg as described in Powder Handling and Processing Volume 2 Number 3, September 1990.

10 The furnace in which the flash calcination in the method according to the first aspect is carried out preferably is of the form described in WO98/03256, the contents of which are incorporated herein by reference. The kaolin particles may be injected into the heating zone of the furnace via a plurality of inlet ports extending radially into the reactor or heating chamber of the furnace whereby the particles are injected into the reactor laterally into the toroidal fluid flow heating zone.

20 By carrying out flash calcination of mineral particulate material in a furnace of the kind described in WO98/03256 it is possible to avoid the problem of build-up of feed material and material produced therefrom and the need for consequent stoppage of the process and cleaning of the operational chamber of the furnace. In such a furnace, the internal constructional features ensure that the temperature of the critical surfaces inside the operational chamber of the furnace are kept below the sintering temperature of

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the feed particulate material to be treated in the furnace thereby avoiding significant accretion of material on such surfaces.

As described earlier, the method according to the first aspect of the present invention gives for flash calcining of kaolin very efficient gas-solid contacting and high impact velocities which in turn provide numerous process benefits including:

(i) Improved energy efficiency; in "massive" prior art structures such as tunnel kilns, multiple hearth kilns (Herreschoff type) and fluid-beds the large structural surface area leads to radiation losses contributing greatly to thermal losses. The toroidal fluid flow furnace allows by its design limitation of such losses, but if required the use of heat recovery systems can further improve the thermal energy efficiency of the system.

(ii) Improved process kinetics. This is achieved through the use of high velocity fluid flow streams which can be tolerated, despite the fineness of the particles being treated, in the toroidal fluid flow furnace. The effect is that all factors which can affect process kinetics are limited. A high thermal gradient is maintained; calcination products (eg water) are driven away as they form and the insulating gas layer which surrounds particles is thinned continuously.

(iii) Improved product quality control; the rapid processing rate enabled by the factors described above

allows the furnace to be a compact unit with a small amount of material in the processing zone at any one time (eg for a 5 tph plant approximately 25 kg needs to be in processing chamber). Any variation in product
5 quality can be corrected by varying processing conditions with a rapid feedback of the effect of changes made.

The present invention is especially beneficial in the flash calcination of hydrated kaolin clays such as
10 kaolinitic clays, eg containing at least 50 per cent by weight hydrated kaolin, eg obtained from china clay or ball clay. By use of the present invention calcined kaolin material can be produced in which voids having a more uniform size and spatial distribution through the
15 particles than those produced by prior art methods can be obtained and this beneficially gives better control over the quality of the product.

The treated particulate material may comprise a material which for example forms at least 90%, eg at
20 least 98% by weight kaolinite. The kaolin particulate material which is to be treated by the method of the invention may have been treated by known beneficiation procedures to have suitable starting properties. The material may be comminuted eg by grinding or milling to
25 have a suitable particle size distribution and particle dispersion. The feed particles employed may be substantially all smaller than 50 μ m. The mean particle size by weight may be in the range 0.5 μ m to 15 μ m. The feed particles may for example have a particle size

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distribution such that at least 50% by weight has an average particle size less than $2\mu\text{m}$. The treated particulate flash calcined kaolin material extracted from the chamber of the furnace may be cooled and
5 treated by one or more known procedures, eg comminution, eg milling to break down aggregates and/or particle size classification, eg using a cyclone.

In general, the particle size distribution which may be obtained for the flash calcined product may be
10 similar to that of the feed material. This is another benefit of the invention.

Quite unexpectedly, the specific gravity or density of products obtained by such dehydroxylation of hydrated kaolin using the method according to the first
15 aspect of the invention can be lower than those obtained by prior art flash calcination methods. For example, flash calcined kaolins having a specific gravity of less than 2.04, in some cases below 2.02, even below 2.00 can be obtained. This is highly
20 beneficial in applications wherein the product is to be used as filler or extender material added to a host material and it is desirable to minimise the specific gravity so that more of the added material can be employed without increasing the weight and reducing the
25 strength of the host material.

An example of such application in which the specific gravity is important in this way is the use of the flash calcined mineral particles for adding to

paints and polymers and latex coating materials as fillers and extenders.

Products obtained by use of the method according to the first aspect which are flash calcined kaolins for example, may therefore be especially useful as high opacity, low specific gravity extenders for adding to paints. The lower specific gravity allows the paint manufacturer to replace more of the expensive pigment TiO_2 , normally employed as opacifier in paints, with the less expensive flash calcined kaolin. The flash calcined kaolin may comprise up to 40% by weight of the paint composition, the amount depending on the type of paint.

According to the present invention in a second aspect there is provided a flash calcined mineral particulate material, eg kaolin, produced by the method according to the first aspect.

The product may have the properties defined earlier and in the later claims.

Embodiments of the present invention will now be described by way of example with reference to the following illustrative examples.

EXAMPLE

A kaolin having the following composition was treated in a furnace of the kind described in WO98/03256.

	Constituent	Weight Percentage
	SiO ₂	48
	Al ₂ O ₃	37
	Other oxides	2
5	(Loss on Ignition	13)

The kaolin was treated in the furnace by flash calcining at a control temperature of 970°C in two separate runs using a residence time of less than 0.5sec and a heating rate temperature gradient of
10 >10⁴°C.sec⁻¹.

The products after flash calcining showed the following properties:

	Run 1	Specific Gravity	1.99
		Brightness	89.4
15		Yellowness	3.8
		Percentage of particles less than 2µm in size	62.3
		(as measured by Sedigraph 5100 machine)	
	Run 2	Specific Gravity	1.98
20		Brightness	89.4
		Yellowness	3.7
		Percentage of particles less than 2µm in size	62.2
		(as measured by Sedigraph 5100 machine)	

25 The products were suitable for use in paint compositions.

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EXAMPLE 2

Paint compositions could be made in a known way, eg by mixing the required ingredients in a blender. A typical matt emulsion formulation which could be made using the flash calcined clay produced as in Example 1, is as follows:

	<u>Ingredient</u>	<u>Weight percentage</u>
10	water	12.7
	TiO ₂	15.0
	calcined kaolin	10.0
	chalk	14.0
	dispersant	0.4
15	ammonia solution	0.1
	defoamer	0.2
	biocide	0.1
	thickening agent	18.0
	20% sodium hexametaphosphate solution	0.8
20		

The above ingredients may be mixed in a blender with a blade speed of 4000 revs per minute, after which the following are added:

25	propylene glycol	0.8
	coalescing solvent	1.5

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- 15 -

The mixture formed may be mixed for 5 minutes at a blade speed of 1500 revs per minute, after which the following are added:

5	emulsion resin	18.2
	water	8.2
		<hr/>
		100.0

10 The mixture formed is further mixed at 1500 revs per minute.

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CLAIMS

1. A method of heat treating kaolin particles which includes the steps of establishing in a furnace a heating zone suitable to calcine the particles and passing the particles rapidly through the heating zone whereby the particles are flash calcined in the heating zone, wherein the furnace is of the kind in which a toroidal fluid flow heating zone is established and the particles are heated in the said heating zone to a temperature of at least 550°C but not greater than 1100°C by application to the particles of a temperature increase rate greater than 10^3 Celsius degrees per second to give a rapid blistering of the particles caused by rapid dehydroxylation of the kaolin and wherein the particles have a residence time of less than 1 second in the said toroidal fluid flow heating zone.
2. A method according to claim 1 and wherein the temperature increase rate of the kaolin particles in the heating zone is at least 5×10^3 Celsius degrees per second.
3. A method according to claim 2 and wherein the residence time of the particles in the heating zone is less than 0.5 second.
4. A method according to claim 1, 2 or 3 and wherein the kaolin particles are delivered into the heating zone dispersed from one another in a carrier fluid.

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5. A method according to claim 4 and wherein the carrier fluid comprises air.
6. A method according to claim 4 or claim 5 and wherein the density of particles in the carrier fluid
- 5 is substantially as high as possible.
7. A method according to any one of the preceding claims and wherein the calcination is carried out at a temperature of from 900°C to 1050°C.
8. A method according to any one of the preceding
- 10 claims and wherein at least 50% by weight of the particles to be treated are kaolinite.
9. A method according to claim 8 and wherein at least 90% by weight of the particles to be treated are kaolinite.
- 15 10. A flash calcined kaolin particulate material produced by the method claimed in any one of the preceding claims.
11. A material according to claim 10 and which comprises kaolinite particles which have been rapidly
- 20 dehydroxylated to have uniformly spaced and sized blisters.
12. A material as in claim 10 or claim 11 and which comprises a flash calcined kaolin having a specific gravity of less than 2.04.
- 25 13. A material according to any one of claims 10 to 12 and wherein the material has the following properties:
- powder brightness greater than 85 ISO
 - yellowness less than 4 ISO
 - specific gravity less than 2.2.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/03426

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01B33/40 B01J8/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MEINHOLD R H ET AL: "Comparison of the kinetics of flash calcination of kaolinite in different calciners" CHEM ENG RES DES PART A TRANS INST CHEM ENG;CHEMICAL ENGINEERING RESEARCH & DESIGN, PART A: TRANSACTIONS OF THE INSTITUTE OF CHEMICAL ENGINEERS JAN 1994, vol. 72, no. A1, January 1994, pages 105-113, XP002091435 see page 108, figure 6 see page 111, right-hand column - page 112	1,2,4-6, 8-11
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/03426

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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